REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 22238.19-CH	2. GOVT ACCESSION NO. NA	3. RECIPIENT'S CATALOG NUMBER NA
4. TITLE (and Subtitle) Theoretical Studies of the Chemical Dynamics of Unimolecular Processes		5. TYPE OF REPORT & PERIOD COVERED Final Report June 1, 1985 - May 31, 1988
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Donald L. Thompson		8. CONTRACT OR GRANT NUMBER(s) DAAG29-85-K-0039
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Oklahoma State University Stillwater, OK 74078		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NA
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211		12. REPORT DATE July 19, 1988
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this research program was to develop computational methods and carry out calculations to investigate the chemical dynamics of large molecules of interest as energetic materials. Classical dynamics studies were made of the intramolecular vibrational energy redistribution and unimolecular reactions in a wide variety of polyatomic molecules, including benzene, toluene, dimethylnitramine, hydrogen peroxide, HONO, and methyl nitrite. These studies are described in this report.

continued

20. ABSTRACT CONTINUED

The technical personnel who contributed to the research on this project include the PI, three postdoctoral research associaties, seven graduate students, one undergraduate student, and a visiting student from Europe. At least twenty publications in refereed journals, one M.S. thesis, and one Ph.D. thesis resulted from the research. The PI gave 25 invited talks at conferences, DoD laboratories, and universities on the research.

FINAL REPORT

Theoretical Studies of the Chemical Dynamics of Unimolecular Processes

AUTHOR OF REPORT:

Donald L. Thompson
Department of Chemistry
Oklahoma State University
Stillwater, Oklahoma 74078

TABLE OF CONTENTS

Abstract

The purpose of this research program was to develop computational methods and carry out calculations to investigate the chemical dynamics of large molecules of interest as energetic materials. Classical dynamics studies were made of the intramolecular vibrational energy redistribution and unimolecular reactions in a wide variety of polyatomic molecules, including benzene, toluene, dimethylnitramine, hydrogen peroxide, HONO, and methyl nitrite. These studies are described in this report.

The technical personnel who contributed to the research on this project include the PI, three postdoctoral research associaties, seven graduate students, one undergraduate student, and a visiting student from Europe. At least twenty publications in refereed journals, one M.S. thesis, and one Ph.D. thesis resulted from the research. The PI gave 25 invited talks at conferences, DoD laboratories, and universities on the research.

Personnel

The scientific personnel who participated in this project are:

Dr. Donald L. Thompson, Principal Investigator

Dr. Jerry A. Darsey, Postdoctoral Research Associate
Dr. Yuhua Guan, Postdoctoral Research Associate
Dr. Alexandria Preiskorn, Postdoctoral Research Associate

Karen L. Bintz (M.S., 1987)
Huadong Gai
Nancy S. Gettys
Durvis Hulen
Thomas Sewell
Bobby G. Sumpter (Ph.D., 1987)
Eric P. Wallis

Gillian Lynch, Undergraduate student

Francoise Remacle, Visiting Ph.D. student from the University of Liege, Belgium.

Final Technical Report

We began this research project with the following long-term plan of approach: First, detailed calculations would be performed for several selected polyatomic molecules in order to further develop the computational methods and obtain the understanding of the dynamics necessary to undertake reliable, realistic studies of reactions in large polyatomic molecules. Next, we would carry out explicit dynamics calculations for reactions in molecules such as RDX, TNT, and nitroalkanes.

In the this grant period, we have investigated intramolecular vibrational energy redistribution (IVR), the fundamental behavior of the dynamics, and unimolecular reactions in a variety of polyatomics. We have also explored various approximations and techniques for improving the methods and facilitating the calculations for reactions in large molecules. Because of the importance of the underlying IVR in unimolecular reactions, it was studied in detail. We have made extensive studies of the rates and pathways of energy transfer and of unimolecular reactions in several molecules. We have studied benzene, hydrogen peroxide, nitrous acid, methyl isocyanide, methyl nitrite, and dimethylnitramine. We have investigated the influence of molecular structure, rotation, potential-energy surface (harmonic/anharmonic, couplings, stretch-bend attenuation, etc.), and initial energy distributions on IVR and reactions. The productivity of the program is summarized in terms of publications, theses, and presentations at the end of this report.

We have reported a thorough study of intramolecular energy transfer in DMNA.[1] The intramolecular energy flow out local CH_3 stretching modes of DMNA was studied by using classical trajectories on various potential-energy surfaces. These surfaces were constructed by using the available experimental data augmented by some limited SCF-MO calculations using GUASSIAN-82. One of the purposes of this study was to determine the importance of various features of the potential; for example, we wished to determine the validity of certain approximations, such as harmonic functions for stretches, which might be used to reduce computer time. And, of course, the rates and mechanisms of the energy transfer in DMNA is of basic interest and can help in reaching a better understanding of the unimolecular reactions. Various initial conditions and three different potential-

energy surfaces were investigated in this study. The difference in the two anharmonic potentials used in the study is in the way the torsional potential was represented. In one, the torsional forces were represented by a truncated cosine series and in the other by nonbonding potentials (Lennard-Jones). In the third potential, all the terms were represented by harmonic functions. The potentials all give approximately the experimentally determined normal mode frequencies.

The major features of the energy transfer in DMNA are the same for all three potential-energy surfaces. The energy flow is rapid and irreversible and occurs on a timescale of approximately 0.25 ps. The energy flow out of the excited methyl stretch modes is initially into the bending modes of the same methyl group and then into the other methyl group, flowing first into the bending modes and ultimately into the stretches of the initially unexcited methyl group. While the energy transfer is not strongly dependent on the potential energy surface, there are some minor differences in the results for the various surfaces. The energy transfer is somewhat slower for the anharmonic potential in which the torsional forces are represented by Lennard-Jones potentials between the nonbonded atoms than in the anharmonic potential with the torsional forces given by the truncated cosine series. This comparison was made to check the possibility that the simpler potential (i.e., Lennard-Jones) would suffice in general studies of the dynamics of DMNA. Use of the Lennard-Jones potential reduces the computational time, but is probably less accurate in general. Thus, we have concluded that the cosine series is the more appropriate form to use. The anharmonic potential referred to in the following discuss is the one with the truncated cosine series for the torsional potential.

There are some subtle differences in the energy transfer for the anharmonic potential and the totally harmonic potential. The rate of flow out excited methyl stretch modes is essentially the same for both potentials. There are, however, some significant differences in the details of the energy redistribution even though the final distribution of the energy after 0.5 ps is about the same for both potentials. Thus, the totally harmonic approximation is acceptable if interest is focused only on the overall rate of the loss of energy from an excited methyl group. This conclusion is interesting in light of the results of our studies of benzene,[2] in which we found that it is necessary to

treat at least the excited stretch mode anharmonically when the potential function does not include interaction terms (stretch-stretch and stretch-bend). Such terms are not included in the DMNA potential. An even better approximation for benzene is to treat both the stretch and the associated bending motion anharmonically. In DMNA, the totally harmonic potential (without interaction terms) gives about the same rate for the initial flow of energy from the stretch, but does not give the same results for the flow of energy out of methyl group into the rest of the molecule.

The picture that has emerged from this study is similar to those for other molecules. The bending degrees-of-freedom plan an important role in the intramolecular energy redistribution. The energy flow out of CH stretch modes is directed along a specific pathway into the other methyl group. Rapid energy transfer out of an excited CH stretch appears to be independent of the molecular environment.

The unimolecular reactions of DMNA were also investigated by using classical trajectories on a realistic potential energy surface.[3] All degrees-of-freedom were treated in these calculations. Values of the rate coefficient for the simple N-N bond rupture reaction to give NO_2 were calculated from microcanonical ensembles of trajectories.

The intramolecular energy transfer was examined in the reactive trajectories. The energy flow into the nitro group increases and rapidly reaches a stable value just before the N-N bond is broken. The NO_2 bend initially absorbs much of the energy that flows into the nitro group. After the N-N bond begins to break the energy in the nitro group rapidly exchanges between the bending and stretching modes of the NO_2.

The predominant path for unimolecular reaction in the N-N bond rupture. The CH bond dissociation is precluded by the rapid flow of energy out of the methyl group. There is evidence that the HONO elimination reaction channel may play a small role in the overall decomposition of DMNA on our potential-energy surface. Two percent of the trajectories produced geometric conditions in which a HONO molecule could be formed. This potential does not include the HONO elimination channel. Thus, a more general potential-energy surface that permits the HONO elimination channel was formulated. Preliminary results of the decomposition of DMNA on a potential-energy surface that

includes the NN, CH, ON, and NC bond dissociations and the HONO elimination reaction have been calculated. These results indicate that the HONO elimination reaction is not very important for a random distribution of initial energy but the rate of this reaction is significantly increased by overtone excitation of one of the CH stretches. This is an interesting results and will be the subject of future study. The final energy in the HONO elimination is primarily partitioned into vibrational energy.

The isomerization of methyl isocyanide to methyl cyanide is one of the more thoroughly studied unimolecular reactions. There are several reason why have recently restudied it using classical trajectories.[4] First, the intramolecular dynamics of isomerizations involving large amplitude bending motions is an important basic problem, and this is one of the best known examples. This reaction is particularly interesting since there are CH bonds adjacent to the isomerization reaction coordinate which provide sites for overtone excitation. The possibility of mode selective chemistry has provided a strong stimulus for much of the recent research into intramolecular energy transfer. Unimolecular reaction rates and product energy distributions in keeping with statistical assumptions are most common. However, theoretical calculations have shown that energy flow from a mode often occurs along specific paths. This suggests that initial nonstatistical flow of energy may ultimately be used to direct the course of reactions. Thus, we investigated this behavior in methyl isocyanide.

There have been numerous experimental and theoretical studies of the isomerization of methyl isocyanide. Of most interest to us was the study of the laser-induced isomerization of methyl isocyanide reported by Reddy and Berry.[5-7] They used laser spectroscopic techniques to measure the isomerization rate. They photoisomerized CH_3NC by directly pumping CH overtone states. They obtained Stern-Volmer plots that are linear, except for the one at v=6. At v=6 the rate constants are a factor of five times larger than those predicted by RRKM calculations based on thermal data.[8a] The broad overtone and combination bands observed in CH_3NC were attributed to intramolecular dephasing and redistribution occurring on a timescale of less than 0.1 ps.[5-7]

The isomerization of methyl isocyanide to methyl cyanide has been a prime subject in the testing of the basic validity of RRKM. Rabinovitch and coworkers[8] have carried

out extensive investigations of the thermal reaction of methyl isocyanide. The thermal isomerization of methyl isocyanide is well described by RRKM theory and is considered a prime example of the success of the theory. We have studied it because of the similar to some of the systems of interest in energetic materials and because of the availability of other results with which to compare. It is a good case for checking potential-energy surface formulations. Nitromethane, and perhaps nitrobenzene, undergo similar isomerizations to the nitrite form.

Harris and Bunker[9] carried out the first trajectory study of the isomerization of methyl isocyanide. Harris and Bunker concluded that the reaction is non-RRKM because of slow intramolecular energy transfer. The rate of energy randomization is not competitive with the rate of isomerization. Bunker and Hase[10] also carried out a detailed investigation of the isomerization of CH_3NC using classical trajectories. They concluded that methyl isocyanide isomerizes with lifetime distributions that are nonrandom and strongly dependent upon the initial conditions. The work by Bunker, Harris, and Hase[9-10] suggest that intramolecular vibrational energy redistribution is incomplete on the timescale of the isomerization.

Because of this background, and the availability of some new *ab initio* results on the potential, we re-examined the dynamics of methyl isocyanide. The overtone-induced isomerization of methyl isocyanide to methyl cyanide was studied by using classical trajectories on several potential-energy surfaces. We have used this system to explore the sensitivity of unimolecular reactions to various features of the potential. The several potential-energy surfaces are variations of a potential which we have developed based on available experimental and *ab initio* results.

The trajectory results for simple potentials which neglect stretch-bend interactions show that overtone excitation of a CH stretch to the v=6 level at total energies (including overtone excitation energy) of 75, 125, and 150 kcal/mol does not enhance the rate of isomerization. However, at an initial total energy of 200 kcal/mol, the isomerization rate is enhanced by as much as a factor of three by selective excitation of a CH stretching overtone. However, the mode specificity is sensitive to the potential-energy surface. When a more realistic potential is used in which the bending

force constants are attenuated as a function of the bond lengths or in which nondiagonal quadratic coupling terms are included, the dominant reaction is CH bond dissociation. The rate coefficient for the CH bond dissociation is an order of magnitude greater than the rate of isomerization at 200 kcal/mol. The initial energy flow out of an excited CH stretch is rapid (occurring on a timescale of less than 0.5 ps) and is primarily into the methyl bending modes. The energy that flows into the bending modes does not transfer out over the time period of 5.4 ps that the trajectories were followed. The methyl bending modes which act as an energy "sink".

Hydrogen peroxide is a good example of a large polyatomic molecule, yet it is small enough to allow accurate theoretical studies to be done. Thus, it has been studied extensively by several groups. We[11-15] carried out a series of studies of it by using various restrictions on the dynamics to determine behavior of overtone relaxation and reaction. We have also investigated the basic behavior of the dynamics for various energies, geometry restrictions, and restrictions on the motion. Included in these studies are investigations of three other systems: HCCC, HNNH, and HCCH. In the first study,[11] we investigated relaxation of OH overtones as a function of excitation level for collinear, planar, and nonplanar models of hydrogen peroxide. The relaxation occurs very slowly compared with that of a CH stretch overtone. The second study[12] was a thorough investigation of the dynamics of hydrogen peroxide and the other systems. Power spectra of auto- and cross-correlation functions were used to classify the type of motion for excited local modes and to investigate the energy transfer mechanisms at various excitation levels. Coherency spectra were used to determine the mode-mode interactions and thus the energy transfer mechanism. The onset of chaotic motion in hydrogen peroxide occurs at about 90% of the energy required for dissociation of the OH bond, i.e., well above the limit for O-O bond rupture. By studying restricted models, we determined the influence of various types of modes on the dynamics and energy transfer. For example, it was found in general for the four systems that the chaotic limit is lowered and the rate of energy flow from an excited local stretch mode is enhanced by the presence of bending degrees of freedom. These calculations show that the amount of energy transferred in a given long time (2 or 3 ps) from a local mode is invariant to the number of degrees of

freedom in the chaotic region but it is strong dependent on the number in the quasiperiodic region. However, the initial (for times less than a ps) rate of energy transfer in the chaotic region is substantially increased by the number of degrees of freedom. That is, there is a difference in the behavior of the energy transfer for the two types of motion on a very short time scale, but the energy transfer on the longer time scales is about the same.

We also carried out a series of calculations on unimoleculear dissociation hydrogen peroxide in collaboration with Dr. Uzer at Georgia Tech.[14,15] In these studies we explored mode specificity for overtone excitations of combinations of modes. We found drastically different lifetimes for different combinations of modes.

Recently, we have studied the influence of rotation on the vibrational energy redistribution in hydrogen peroxide and on the rate of O-O bond rupture for initial conditions in which a zeroth-order OH stretch overtone state is excited.[13] We find that there is a substantial effect. The rates of energy transfer and dissociation are increased by factors on the order of 2.5 by including rotation. We have also recently completed a study of the effects of rotation on energy transfer in Benzene[16] and the HONO cis-trans isomerization.[17,18] The effects of rotation on intramolecular dynamics and unimolecular reaction rates have long been a topic of considerable interest. For example, a number of papers have been written on it with reference to RRKM.

HONO is an important product in the initial decomposition of some molecules of interest as energetic materials. It is also interesting from a basic research point of view. The results for hydrogen peroxide have provided a lot of insight into the intramolecular dynamics, energy redistribution, and dissociation Thus, it seemed reasonable to extend these studies to HONO. It is one of the simplest molecules that can undergo cis-trans isomerization and is more general than HOOH since it is not symmetric. The barrier to isomerization is about 9.7 kcal/mol. Thus, it provides a real system for which questions of mode specific excitation influence on reaction can be explored. Based on the results for HOOH and experimental studies on similar systems by Bauer and coworkers[19], it seems reasonable that the intramolecular conversion in HONO would provide a realistic situtation in which nonstatistical effects might be important.

Pimentel and coworkers,[20] and McDonald and Shirk[21] have also published some experimental studies that suggest that HONO will display interesting dynamics effects. Darsey and Thompson[22] carried out *ab initio* SCF-MO calculations to obtain an accurate torsional potential function for HONO. Completely optimized geometries using the 4-31G basis set were used to calculate a potential which was least-squares fit with a cosine series for use in dynamics calculations. The barrier to isomerization on the computed potential is 9.68 kcal/mol. Classical trajectories were then used to investigate *cis-trans* isomerization and intramolecular vibrational energy redistribution.[17] The influence of various initial normal mode excitations were studied. Power spectra were used to examine the dynamics. The rate of *cis-trans* conversion is strongly dependent on the site of initial excitation. The rates for *cis-trans* isomerization is significantly higher than those for *trans-cis*. The results show that the OH stretching mode is only weakly coupled to the other modes. Energy transfer out of overtones of the OH stretch is slow and preferential partitioning of initial energy in that mode leads to a reduced rate of isomerization compared with other initial energy distributions at the same total energy. The HON bend mode interacts with the torsion more strongly than do any of the other modes.

Recently, we have completed a study of the influence of rotation on HONO isomerization.[18] By using a potential with no coupling terms, we can show that there are strong effects of the rotation on the coupling of the kinetic energy. This work is being prepared for publication.

The intramolecular vibrational relaxation and the high-energy spectroscopy have been studied more thoroughly for benzene than most other molecules. From a theoretical standpoint, it has served as prototypical system for investigating the rates and mechanisms by which energy initially localized in CH stretch mode becomes redistributed. A number of people have reported theoretical studies of the IVR in benzene. Because it is well-studied by various methods, it is an excellent molecule to use to investigate various aspect of computational treatments of the full dynamics of large molecules. We have carried out a number of studies of benzene aimed primarily at exploring the details and methods of classical dynamics treatments of large molecules. For example, we have used it to check various approximations for potentials.

A variety of mechanisms have been advanced to explain the rapid rate of intramolecular vibrational relaxation observed subsequent to overtone excitation of CH bonds in benzene. Resonance interactions, especially the Fermi resonance between an excited CH bond and the associated CCH wag, have generally been advanced as instrumental in enchancing the rate of energy transfer from the excited CH bond. Shi and Miller[23] and Cerjan, Shi, and Miller[24] have reported theoretical studies of lineshapes of CH stretch overtones in benzene in which they discuss the decay of energy from the excited CH bond in terms of resonance interactions. Several other theoretical studies have also reported numerical techniques for calculation of CH overtone lineshapes in benzene.[25,26] Sibert et al.[27] have reported classical and quantum mechanical studies that address the decay of energy from overtone excitations of CH bonds in the context of resonance interactions. Stannard and Gelbart[28] reported a theoretical study of intramolecular vibrational energy redistribution in benzene. Reddy, Heller, and Berry[29] proposed and tested several possible mechanisms for energy flow from overtone exitations of CH bonds. Holme and Hutchinson[30] have noted that in polyatomic molecules intramolecular vibrational relaxation occurs much faster than does excitation. As energy is absorbed by a local mode, it is almost simultaniously relaxing into eigenstates which project onto that local mode. This is evident in the classical trajectory calculations by the immediate rapid flow of energy from excited zeroth-order states. Nagy and Hase[31] have reported a classical trajectory study of benzene. More recently, Clarke and Collins[32] have reported trajectory studies of benzene and perdeuterobenzene.

We have reported several classical trajectory studies of CH overtone relaxation in benzene.[2,16,33-35] These studies focus on approximations in potential-energy surface formulations. The purpose was to learn more about where approximation can be made to simplify the calulation of dynamics of large polyatomic molecules. In the first two studies,[2,33] potentials without coupling terms were used. In the first study,[33] we computed trajectories for planar benzene on two types of potential-energy surfaces, harmonic and anharmonic, by using the analytic form of Nagy and Hase, but with different values of the parameters. In the second study,[2] the effect of anharmonicity on the IVR was more fully investigated. We investigated potential-energy surfaces with varying

degrees of anharmonicity to determine which modes can be treated harmonically without affecting the rate of energy transfer. The results show that it is necessary to treat at least the excited stretch mode anharmonically, and a better results is obtained if the wag mode (which interacts most strongly with the stretch) is also treated anharmonically. These results have ramifications for reaction path hamiltonian approaches where a reaction mode is coupled to a harmonic bath.

Following these studies, we investigated to accuracy of a harmonic force field with coupling terms as well as the influence of out-of-plane motion on IVR. The third study[34] employed harmonic potential of the form of the *ab initio* surface developed by Pulay, Forgarasi, and Boggs.[36] The results obtained in this study indicate that energy redistribution in benzene is very rapid, occurring on a timescale of approximately .2 to .3 ps. There appears to be no localization of energy within the molecule on more than a subpicosecond timescale. This is an interesting result because the potentials used in these calculations are harmonic. In our previous studies of benzene using simplier (primarily fewer coupling terms) analytical forms for the potentials it was found that anharmonic potentials were necessary in order to correctly predict the rapid energy transfer out of excited modes. The results for the Pulay *et al.* potential show that the importance of anharmonicity depends on other features of the potential-energy surface. A purely harmonic potential can predict the correct rate of energy transfer in benzene. Obviously, the harmonic approximation is not accurate in some respects at these levels of excitation. Thus, some of the computed properties of the energy transfer, such as the details of the pathways, may not be completely realistic. Nevertheless, it is important to note that the harmonic force field gives the correct behavior for the initial relaxation of the CH stretch overtone.

We also investigated the energy transfer pathways by following the energy in the various normal modes as a function of time. There are two distinct sets of ring modes, the essentially nonparticipating low frequency modes and the higher frequency modes which are integrally involved in the rapid decay of energy from the CH bond. Within the higher frequency range, participating set of modes it appears that the modes which possess the most CCH bend character are more strongly coupled to the excited CH bond. Energy flows

preferentially into these modes and then decays into other ring modes which possess significant ring stretch and deformation character.

The effect of out-of-plane motion on IVR was studied by comparing results for planar and nonplanar benzene. It was found that the inclusion of out-of-plane motion does not appear to enhance the rate of energy flow from an excited CH bond.

We also used classical trajectories to investigate energy relaxation of various excited C-C stretching, CCH bending, and CCC bending normal modes in benzene.[35] These normal modes were initially excited up to about 10,000 cm^{-1}. The calculated relaxation of the excited C-C ring breathing mode is in agreement with the recent experimental results of Chernoff, Myers, and Pruett.[37] In general, the relaxation of the excited normal modes involving C-C stretching, CCH bending, and CCC bending are at least several times slower than the relaxation of the CH stretch local mode. Mode-to-mode energy transfer was also investigated. Only those modes whose frequencies are close to that of the excited mode participate in the energy transfer.

Cis-trans isomerization and IVR in methyl nitrite has also been studied.[38] We have computed an *ab initio* torsional potential and fit it with a cosine series as we did in the case of HONO.[39] Initial conditions for microcanonical distributions of initial energy and CH stretch overtones were investigated. We found that the CH overtone excitations give the same rates as does the equipartitioning of the initial energy. We are currently studying the competing simple bond-rupture reactions to give $CH_3O + NO$ and $CH_3 + NO_2$.

References

1. B. G. Sumpter and D. L. Thompson, J. Chem. Phys. 86, 3301 (1987).

2. K. L. Bintz, D. L. Thompson, and J. W. Brady, Chem. Phys. Lett. 131, 398 (1986).

3. B. G. Sumpter and D. L. Thompson, J. Phys. Chem. 88, 6889 (1988).

4. B. G. Sumpter and D. L. Thompson, J. Chem. Phys. 87, 5809 (1987).

5. K. V. Reddy and M. J. Berry, Chem. Phys. Lett. 52, 111 (1977).

6. K. V. Reddy, R. G. Bray, and M. J. Berry, in *Advances in Laser Chemistry*, edited by A. M. Zewail (Springer, Berlin, 1978), p. 48.

7. K. V. Reddy and M. J. Berry, Faraday Dicuss. Chem. Soc. 67, 188 (1979).

8. (a) F. W. Schneider and B. S. Rabinovitch, J. Am. Chem. Soc. 84, 4215 (1962); (b) B. S. Rabinovitch, P. W. Gilderson, and F. W. Schneider, J. Am. Chem. Soc. 87, 158 (1965); (c) S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, J. Phys. Chem. 74, 3160 (1970); (d) F.-M. Wang, T. Fujimoto, and B. S. Rabinovitch, J. Phys. Chem. 76, 1935 (1972); (e) F.-M. Wang, T. Fujimoto, and B. S. Rabinovitch, Can. J. Chem. 50, 3251 (1972); (f) F.-M. Wang and B. S. Rabinovitch, J. Phys. Chem. 78, 863 (1974).

9. H. H. Haris and D. L. Bunker, Chem. Phys. Lett. 11, 433 (1971).

10. D. L. Bunker and W. L. Hase, J. Chem. Phys. 59, 4621 (1973); 69, 4711(E) (1978).

11. B. G. Sumpter and D. L. Thompson, J. Chem. Phys. 82, 4557 (1985).

12. B. G. Sumpter and D. L. Thompson, J. Chem. Phys. 86, 2805 (1987).

13. B. G. Sumpter and D. L. Thompson, Chem. Phys. Letters, in press.

14. T. Uzer, B. D. MacDonald, Y. Guan, and D. L. Thompson, "Theroetical Studies of Mode-Specificity in the Dissociation of Overtone-Excited Hydrogen Peroxide," Chem. Phys. Lett., submitted.

15. T. Uzer, B. D. MacDonald, Y. Guan, and D. L. Thompson, "Theroetical Studies of Mode-Specificity in the Dissociation of Overtone-Excited Hydrogen Peroxide," J. Chem. Phys., to be submitted.

16. Y. Guan and D. L. Thompson, unpublished.

17. Y. Guan, G. C. Lynch, and D. L. Thompson, J. Chem. Phys. 87, 6957 (1987).

18. Y. Guan and D. L. Thompson, "Influence of Rotation on Dissociation of HONO," J. Chem. Phys., to be submitted.

19. See, for example: (a) S. H. Bauer and N. S. True, J. Phys. Chem. 84, 2507 (1980); (b) K. I. Lazaar and S. H. Bauer, J. Phys. Chem. 88, 3052 (1984); (c) D. B. Borchardt and S. H. Bauer, J. Chem. Phys. 85, 4980 (1986).

20. (a) J. D. Baldeschwieler and G. C. Pimentel, J. Chem. Phys. 33, 1008 (1960); (b) R. T. Hall and G. C. Pimentel, J. Chem. Phys. 38, 1889 (1963).

21. (a) P. A. McDonald and J. S. Shirk, J. Chem. Phys. 77, 2355 (1982);
    (b) A. E. Shirk and J. S. Shirk, Chem. Phys. Lett. 97, 549 (1983).

22. J. A. Darsey and D. L. Thompson, J. Phys. Chem. 91, 3168 (1987).

23. S. Shi and W. H. Miller, Theor. Chim. Acta 68, 1 (1985)

24. C. J. Cerjan, S. Shi, and W. H. Miller, J. Phys. Chem. 86, 2244 (1982)

25. D. F. Heller and S. Mukamel, J. Chem. Phys. 70, 463 (1979).

26. V. Buch, R. B. Gerber, and M. A. Ratner, J. Chem. Phys. 81, 3393 (1984).

27. (a) E. L. Sibert, J. T. Hynes, and W. P. Reinhardt, J. Chem. Phys. 81, 1135 (1982);
    (b) E. L. Sibert, W. P. Reinhardt, and J. T. Hynes, J. Chem. Phys. 81, 1115
    (1984); (c) E. L. Sibert, J. S. Hutchinson, J. T. Hynes, and W. P. Reinhardt,
    in Ultrafast Phenomena IV, edited by D. H. Auston and K. B. Eisenthal
    (Springer-Verlag, New York, 1984), p. 336; (d) E. L. Sibert, W. P. Reinhardt,
    and J. T. Hynes, Chem. Phys. Lett. 92, 455 (1982).

28. P. R. Stannard and W. M. Gelbart, J. Phys. Chem. 85, 3592 (1981).

29. K. V. Reddy, D. F. Heller, and M. J. Berry, J. Chem. Phys. 76, 2814 (1982).

30. T. A. Holme and J. S. Hutchinson, J. Chem. Phys. 84, 5455 (1986).

31. P. J. Nagy and W. L. Hase, Chem. Phys. Letters 54, 73 (1978); Erratum: 58,
    482 (1978).

32. (a) D. L. Clarke and M. A. Collins, J. Chem. Phys. 86, 6871 (1987);
    (b) ibid. 87, 5312 (1987).

33. K. L. Bintz, D. L. Thompson, and J. W. Brady, J. Chem. Phys. 85, 1848 (1986).

34. K. L. Bintz, D. L. Thompson, and J. W. Brady, J. Chem. Phys. 86, 4411 (1987).

35. Y. Guan and D. L. Thompson, J. Chem. Phys. 88, 2355 (1988).

36. P. Pulay, G. Fogarasi, and J. E. Boggs, J. Chem. Phys. 74, 3999 (1981).

37. D. A. Chernoff, J. D. Myers, and J. G. Pruett, J. Chem. Phys. 85, 3732 (1986).

38. A. Preiskorn and D. L. Thompson, "Cis-Trans Isomerization of Methyl nitrite,"
    J. Phys. Chem., to be submitted.

39. J. A. Darsey and D. L. Thompson, Chem. Phys. Letters 145, 523 (1988).

Publications, Theses, and Oral Presentations

Publications .

The following is a list of the publications that have resulted from this research:

1. D. W. Noid and B. G. Sumpter, "New Method to Calculate Surfaces of Section," Chem. Phys. Letters 121, 187-190 (1985).

2. K. L. Bintz, D. L. Thompson, and J. W. Brady, "Classical Dynamics Study of Intramolecular Energy Flow in Benzene," J. Chem. Phys. 85, 1848-1853 (1986).

3. D. W. Noid and B. G. Sumpter, "Method for Semiclassical Calculation of Grid of Eigenvalues," Chem. Phys. Letters 126, 181-184 (1986).

4. K. L. Bintz, D. L. Thompson, and J. W. Brady, "Influence of Anharmonicity of "Bath" Modes on Intramolecular Energy Transfer From a Local Mode," Chem. Phys. Lett. 131, 398-402 (1986).

5. B. G. Sumpter and D. L. Thompson, "Studies of the Intramolecular Dynamics of Model Polyatomic Molecules, " J. Chem. Phys. 86, 2805-2817 (1987).

6. B. G. Sumpter and D. L. Thompson, "Intramolecular Vibrational Relaxation of CH Stretch Overtones in Dimethylnitramine," J. Chem. Phys. 86, 3301-3310 (1987).

7. K. L. Bintz, D. L. Thompson, and J. W. Brady, "Intramolecular Vibrational Relaxation of CH Stretch Overtones in Benzene," J. Chem. Phys. 86, 4411-4417 (1987).

8. J. A. Darsey and D. L. Thompson, "*Ab Initio* Molecular Orbital Calculation of the HONO Torsional Potential," J. Phys. Chem. 91, 3168-3171 (1987).

9. B. G. Sumpter, D. L. Thompson, and D. W. Noid, "The Effect of Resonances on Collisional Energy Transfer," J. Chem. Phys. 87, 1012-1021 (1987).

10. B. G. Sumpter and D. L. Thompson, "Intramolecular Dynamics of Overtone-Induced Isomerization of Methyl Isocyanide," J. Chem. Phys. 86, 3301-3310 (1987).

11. Y. Guan, G. C. Lynch, and D. L. Thompson, "Mode Specificity in the *Cis-Trans* Isomerization of HONO," J. Chem. Phys. 87, 6957-6966 (1987).

12. Y. Guan and D. L. Thompson, "Relaxation of Excited Normal Modes in Benzene," J. Chem. Phys. 88 2355-2360 (1988).

13. J. A. Darsey and D. L. Thompson, "*Ab Initio* Molecular Orbital Calculation of the Methyl Nitrite Torsional Potential," Chem. Phys. Letters 145, 523-528 (1988).

14. B. G. Sumpter and D. L. Thompson, "Unimolecular Reaction Dynamics of Dimethylnitramine," J. Phys. Chem. 88, 6889-6897 (1988).

15. B. G. Sumpter and D. L. Thompson, "Influence of Rotation on the Intramolecular Dynamics of Hydrogen Peroxide," Chem. Phys. Letters, in press.

16. T. Uzer, B. D. MacDonald, Y. Guan, and D. L. Thompson, "Theroetical Studies of Mode-Specificity in the Dissociation of Overtone-Excited Hydrogen Peroxide," Chem. Phys. Lett., submitted.

17. Y. Guan and D. L. Thompson, "Mode Specificity and the Influence of
Rotation in *Cis-Trans* -Trans Isomerization
Dissociation in HONO," J. Chem. Phys., to be submitted.

18. A. Preiskorn and D. L. Thompson, "*Cis-Trans* Isomerization of Methyl Nitrite,"
J. Phys. Chem., to be submitted.

19. A. Preiskorn and D. L. Thompson, "Classical Trajectory Study of Simple
Bond Rupture Reactions in Methyl Nitrite," J. Phys. Chem., to be submitted.

20. T. Uzer, B. D. MacDonald, Y. Guan, and D. L. Thompson, "Theroetical Studies of
Mode-Specificity in the Dissociation of Overtone-Excited Hydrogen Peroxide,"
J. Chem. Phys., to be submitted.

Theses

On Ph.D. student and one M.S. student, who were supported by this
program, completed degrees during the first grant period:

Bobby G. Sumpter, Theoretical Investigations of Intramolecular Energy
Transfer in Polyatomic Molecules. (Ph.D., December 1986)

Karen L. Bintz, Classical Dynamics Study of Intramolecular Energy
Transfer in Benzene. (M.S., December 1986)

Presentations

The PI presented talks on this research at the following meetings, workshops, and
universities:

1. Chemical Dynamics Seminar, Chemistry Department, University of California,
Berkeley, August 6, 1984.

2. Department of Chemistry, Tarleton State University, Stephenville, Texas,
October 15, 1984.

3. Department of Chemistry, Northeastern State University, Tahlequah, Oklahoma,
November 8, 1984.

4. Chemistry Department, Oak Ridge National Laboratory, Oak Ridge, Tenn., January
28, 1985.

5. Chemistry Department, University of Arkansas, Little Rock, February 11, 1985.

6. Workshop on the combustion of nitramines, sponsored by the Army Research Office
at Sandia-Livermore, June 9-11, 1986.

7. Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, October 21,
1986.

8. 1986 Sigma Xi Lecture, Oklahoma State University, Stillwater, December 4, 1986.

9. Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM, January 7,
1987.

10. Workshop on New Directions in Energetic Materials, The Frank J. Seiler Research
Laboratory, U.S. Air Force Academy, Colorado Springs, March 12, 1987.

11. Society of Physics Students at Central State University, Edmond, Oklahoma, April 15, 1987.

12. CECAM workshop on Vibrational Predissociation, Orsay, France, June 15-26, 1987.

13. Department of Chemistry, Iowa State University, Ames, October 9, 1987.

14. Department of Chemistry, University of Mississippi, November 6, 1987.

15. Symposium on "Structure, Dynamics, and Spectroscopy," at the Southwest Regional ACS Meeting, Little Rock, Arkansas, December 2-4, 1987.

16. Department of Chemistry, University of Nebraska, Omaha, January 29, 1988.

17. Picatinny Arsenal, Dover, New Jersey, March 11, 1988.

18. Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, March 11, 1988.

19. 9th Rocky Mountain ACS Meeting, Las Vegas, March 27-30, 1988.

20. University of California, Berkeley, April 1, 1988

22. Department of Chemistry, University of Missouri, Kansas City, April 6, 1988.

23. Department of Chemistry, University of Texas, Dallas, April 27, 1988.

24. JANNAF Conference on Kinetic and Related Aspects of Propellant Combustion Chemistry, Silver Spring, Maryland, May 2-4, 1988.

25. Frank J. Seiler Research Laboratory, U.S. Air Force Academy, June 16, 1988.

END

DATE

FILMED

DTIC

11- 88